

Chapter-14

Lesson-1

I – Reaction Rates

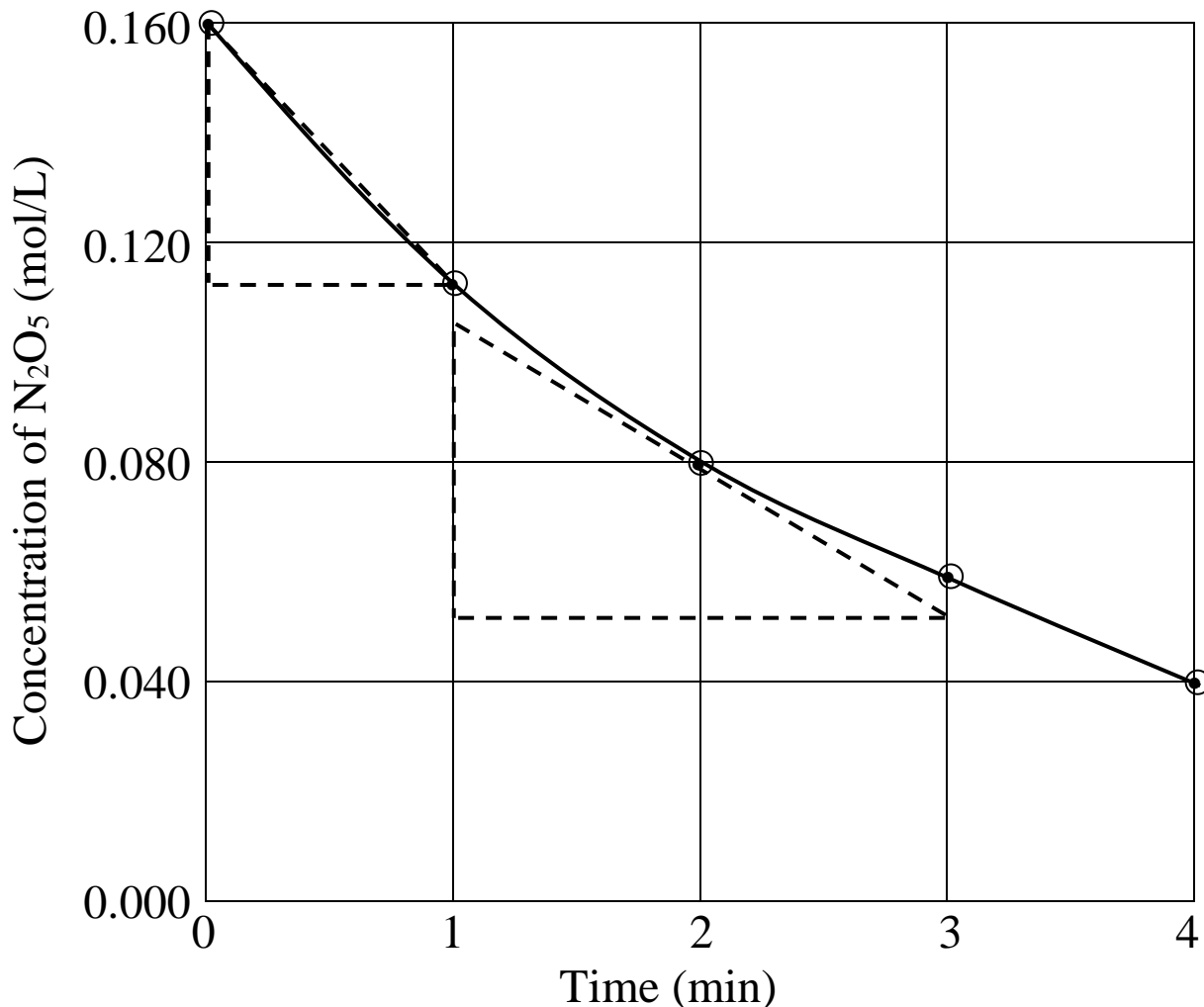
- The rate of reaction is a ***positive quantity*** that tells us how the concentration (M) of a reactant (product) is changing with time (S).

$$\text{Rate} = - \frac{\Delta[\text{reactant}]}{\Delta t} \quad \text{or} \quad \text{Rate} = + \frac{\Delta[\text{product}]}{\Delta t}$$

Besides M/s, the units for reaction rate can be atm/s, mmHg/min, or torr/hr.

- The rate of reaction can be determined by measuring concentration of reactant as a function of time and graphing the data.

$2 \text{N}_2\text{O}_{5(g)} \rightarrow 4 \text{NO}_{2(g)} + \text{O}_{2(g)}$ (at 67°C)					
Time (min)	0	1	2	3	4
$[\text{N}_2\text{O}_5]$ M	0.160	0.113	0.080	0.056	0.040



- The **average reaction rate** is equal to ...

$$\text{Average Rate} = - \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

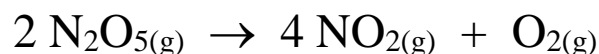
which is the negative slope of the line that connects any two points on the curve.

2 N₂O_{5(g)} → 4 NO_{2(g)} + O_{2(g)} (at 67°C)					
Time (min)	0	1	2	3	4
[N ₂ O ₅] M	0.160	0.113	0.080	0.056	0.040
Average Rate (M/min)	0.047				
		0.033			
			0.024		
				0.016	
	0.030				

- The **instantaneous reaction rate** is equal to the negative slope of the line that is tangent to the curve at a point in time.

2 N₂O_{5(g)} → 4 NO_{2(g)} + O_{2(g)} (at 67°C)		
Time (min)	at 0	at 2
[N ₂ O ₅] M	0.160	0.080
Instantaneous Rate (M/min)	≈0.053	≈0.027

- To equate the reaction rates determined from the changing concentrations of reactant or product, the stoichiometry of the reaction must be considered. In the reaction,



two moles of N₂O_{5(g)} disappear for every four moles of NO_{2(g)} that appear and for every one mole of O_{2(g)} that appears.

Thus to equate the reaction rates, the rate of change in concentration of a particular species is divided by its coefficient.

$$\text{Rate} = - \frac{1}{2} \frac{[\text{N}_2\text{O}_5]}{\Delta t} = + \frac{1}{4} \frac{[\text{NO}_2]}{\Delta t} = + \frac{1}{1} \frac{[\text{O}_2]}{\Delta t}$$

At 2 min., the rate at which NO_{2(g)} appears is ≈0.054 M/min.

II – Rate Laws

- The reaction rate depends only on the reactant concentrations and the temperature. An equation which shows how the rate depends on the concentrations of reactants, is called a **rate law**.

For the reaction, $X \rightarrow Y + Z$

$$\text{Rate} = k[X]^m$$

For the reaction, $A + B \rightarrow C + D$

$$\text{Rate} = k[A]^m[B]^n$$

- The proportionality constant k , called the **rate constant**, is specific for a given reaction at a given temperature but does not change as the reaction proceeds.
- The exponents m and n , called **reaction orders**, define how the rate is affected by reactant concentrations.
 - If the rate does not depend on reactant concentration, then **reaction order** is 0.
 - If the rate doubles as reactant concentration doubles, then **reaction order** is 1.
 - If the rate quadruples as reactant concentration doubles, then **reaction order** is 2.

Q1: From the data below, determine (i) the reaction order and (ii) the rate constant for the reaction, $N_2O_{5(g)} \rightarrow 4 NO_{2(g)} + O_{2(g)}$.

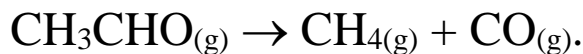
$[N_2O_5]$ (M)	0.160	0.080	0.040
Rate (M/min)	0.056	0.028	0.014

A1: (i) Since the reaction rate halves as the concentration of N_2O_5 halves, then the reaction is 1st order with respect to N_2O_5 .
Thus... $\text{Rate} = k [N_2O_5]^1$

$$(ii) \quad k = \frac{\text{Rate}}{[N_2O_5]^1} \rightarrow k = \frac{0.056 \text{ M/min}}{[0.160 \text{ M}]^1} \rightarrow \boxed{k = 0.35 \text{ min}^{-1}}$$

Rate constants have units that must be evaluated in every case!

Q2: From the data below, determine (i) the reaction order and (ii) the rate constant for the following reaction:



Trial	1	2	3
[CH ₃ CHO]	0.500	0.350	0.200
Rate (M/s)	0.500	0.245	0.080

A2: The reaction order CANNOT be as easily determined from the data.

(i) **Using the data from trials 1 and 2:** (any 2 trials would work)

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^m$$

$$\begin{array}{l} \text{Rate}_1 = k[\text{CH}_3\text{CHO}]^m \rightarrow \frac{0.500}{0.245} = \frac{k[0.500]^m}{k[0.350]^m} \\ \text{Rate}_2 = k[\text{CH}_3\text{CHO}]^m \end{array}$$

$$\frac{0.500}{0.245} = \left(\frac{[0.500]}{[0.350]} \right)^m \rightarrow 2.04 = 1.43^m$$

$$\ln(2.04) = \ln(1.43^m) \rightarrow \ln(2.04) = m \cdot \ln(1.43)$$

$$m = \frac{\ln(2.04)}{\ln(1.43)} \rightarrow \boxed{m = 2}$$

(ii) **Using the data from trial 3:** (any trial would work)

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^m$$

$$0.080 = k[0.200]^2$$

$$\boxed{k = 2.00 \text{ M}^{-1} \cdot \text{s}^{-1}}$$

- For reactions with more than one reactant, the overall reaction order is equal to the sum of the individual reaction orders.

For the reaction, $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

The *overall reaction order* is equal to **m + n!**

Q3: One of the many reactions that occurs in an automobile is



Use the following data to determine (i) the reaction order in NO_2 , (ii) the reaction order in CO , (iii) the overall reaction order, and (iv) the value of the rate constant.

Experiment	Initial Rate (M/s)	Initial $[\text{NO}_2]$ (M)	Initial $[\text{CO}]$ (M)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

A3: *The reaction orders CAN be as easily determined from the data.*

$$\begin{aligned} \text{(i)} \quad \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}_2]^m[\text{CO}]^n}{k[\text{NO}_2]^m[\text{CO}]^n} = \frac{[\text{NO}_2]^m}{[\text{NO}_2]^m} \end{aligned}$$

$$\frac{(0.080)}{(0.0050)} = \frac{[0.40]^m}{[0.10]^m} = \left[\frac{0.40}{0.10} \right]^m$$

$$16 = 4.0^m \quad \text{thus} \quad \boxed{m = 2} \quad \text{the reaction is } \underline{2^{\text{nd}}} \text{ order in } \text{NO}_2.$$

$$\begin{aligned} \text{(ii)} \quad \frac{\text{Rate}_3}{\text{Rate}_1} &= \frac{k[\text{NO}_2]^m[\text{CO}]^n}{k[\text{NO}_2]^m[\text{CO}]^n} = \frac{[\text{CO}]^n}{[\text{CO}]^n} \end{aligned}$$

$$\frac{(0.0050)}{(0.0050)} = \frac{[0.20]^n}{[0.10]^n} = \left[\frac{0.20}{0.10} \right]^n$$

$$1.0 = 2.0^n \quad \text{thus} \quad \boxed{n = 0} \quad \text{the reaction is } \underline{\text{zero}} \text{ order in } \text{CO}$$

(iii) *The reaction is overall 2nd order!*

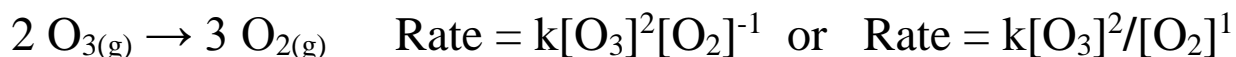
$$\text{(iv)} \quad \text{Rate}_1 = k[\text{NO}_2]^m[\text{CO}]^n$$

$$0.0050 = k[0.10]^2[0.10]^0$$

$$0.0050 = k(0.010)$$

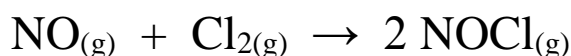
$$\boxed{k = 0.50 \text{ M}^{-1} \text{ s}^{-1}}$$

- Reaction orders can be **negative**! A negative reaction order means that the reaction slows down as the concentration increases.
- For the decomposition of ozone in the upper atmosphere ...



the reaction is second order with respect to ozone but is negative one order with respect to oxygen gas. As more and more O_2 is produced, the reaction slows down.

Q4: Use the following data to determine (i) the reaction order in NO, (ii) the reaction order in Cl_2 , (iii) and the overall reaction order, and (iv) the value of the rate constant.



Experiment	Initial Rate (M/min)	Initial [NO] (M)	Initial [Cl_2] (M)
1	0.18	0.10	0.10
2	0.36	0.10	0.20
3	1.45	0.20	0.20

A4: *The reaction orders CAN be as easily determined from the data.*

(i) **Using the data from trials 2 and 3:**

$[\text{Cl}_2]$ is constant. As $[\text{NO}]$ doubles, the rate quadruples so the reaction is 2nd order with respect to NO.

(ii) **Using the data from trials 1 and 2:**

$[\text{NO}]$ is constant. As $[\text{Cl}_2]$ doubles, the rate doubles so the reaction is 1st order with respect to Cl_2 .

(iii) $\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]^1$

(iv) $\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]^1$

$$1.45 = k[0.20]^2[0.20]^1$$

$$\boxed{k = 180 \text{ M}^{-2} \text{ min}^{-1}}$$

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Lesson-2

III – Change of Concentration with Time

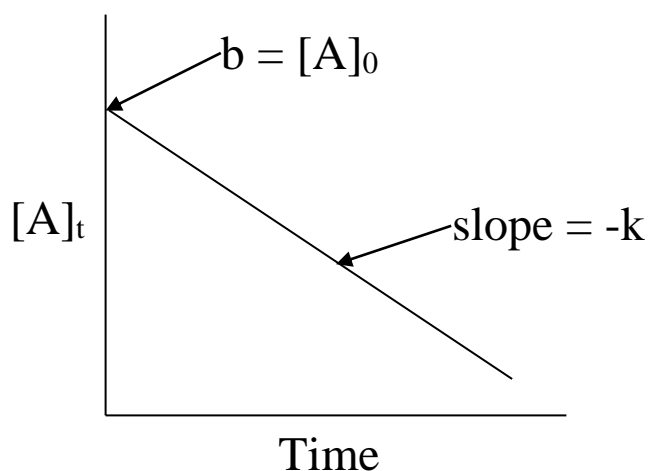
A) Zero Order Reactions

$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]^0 = k$$

Integrating over time gives...

$$[A]_t - [A]_0 = -kt$$

$$\begin{array}{ccccccc} [A]_t & = & -kt & + & [A]_0 \\ \uparrow & & \uparrow\uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$



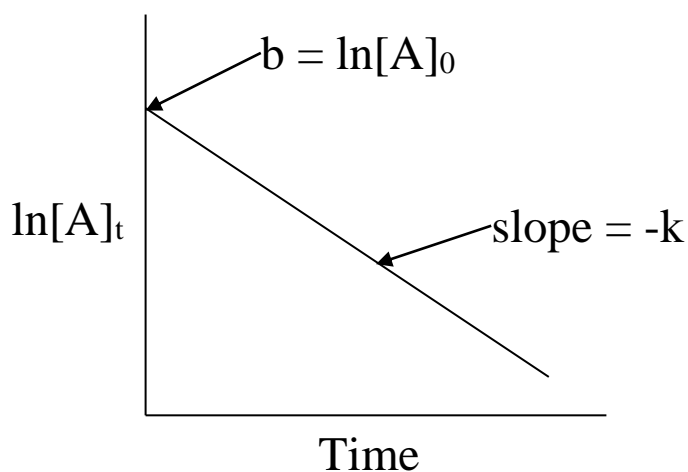
B) First Order Reactions

$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]^1$$

Integrating over time gives...

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\begin{array}{ccccccc} \ln[A]_t & = & -kt & + & \ln[A]_0 \\ \uparrow & & \uparrow\uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$



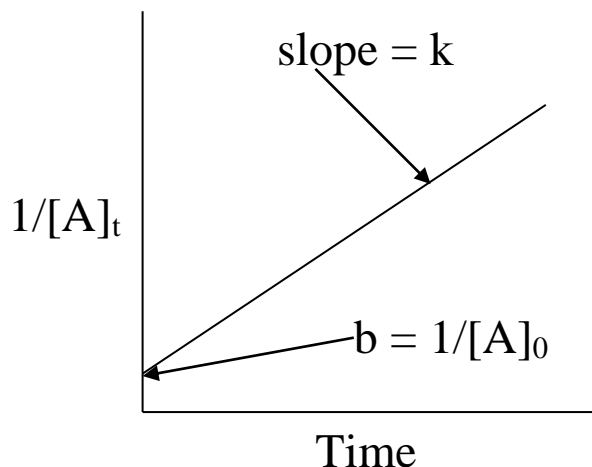
C) Second Order Reactions

$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]^2$$

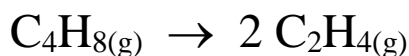
Integrating over time gives...

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\begin{array}{ccccccc} \frac{1}{[A]_t} & = & kt & + & \frac{1}{[A]_0} \\ \uparrow & & \uparrow\uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$



Q1: At 1000°C, cyclobutane decomposes to give two molecules of ethylene (ethene).



If the rate constant is 87 s^{-1} , and the initial $[\text{C}_4\text{H}_8]$ concentration is 2.00 M, then ...

- determine the reaction order and the appropriate integrated rate equation.
- calculate the $[\text{C}_4\text{H}_8]$ concentration after 0.010 s.
- calculate how long it takes for $[\text{C}_4\text{H}_8] = 2.00 \times 10^{-9} \text{ M}$.

A1: (i) Since the units of the rate constant are s^{-1} , then the reaction order is 1. For a 1st order reaction, $\ln[A]_t - \ln[A]_0 = -kt$

$$(ii) \ln[X] - \ln[2.00] = (-87)(0.010) = -0.87$$

$$X = 0.84 \text{ M}$$

$$(iii) \ln[2.00 \times 10^{-9}] - \ln[2.00] = (-87)(X)$$

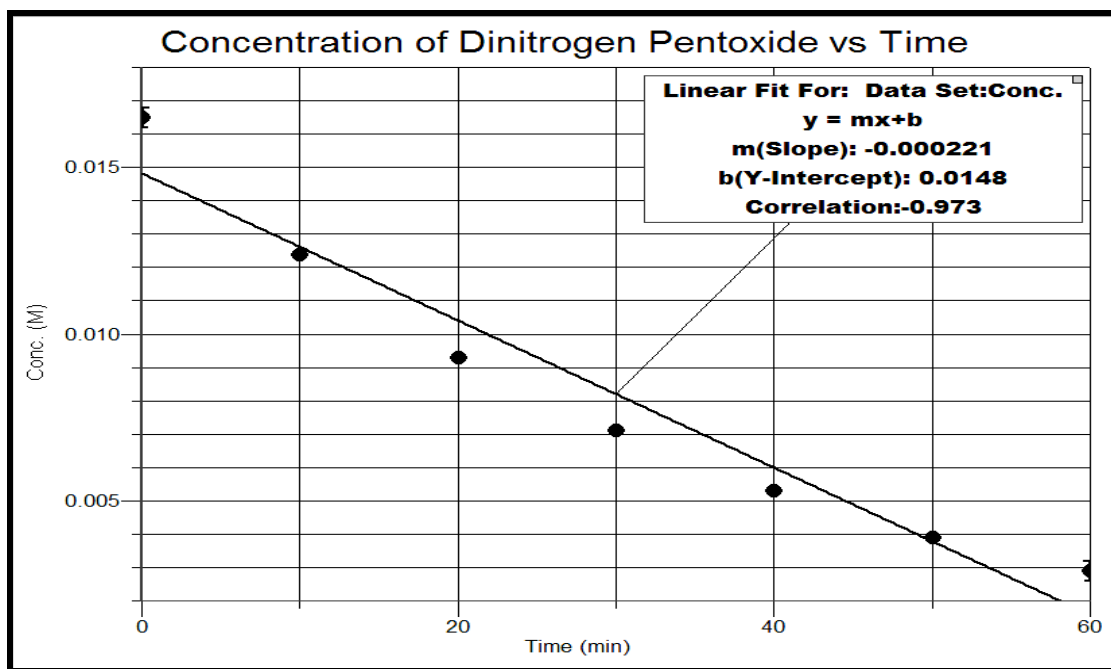
$$X = 0.24 \text{ s}$$

D) Using Integrated Rate Laws to Find Reaction Order

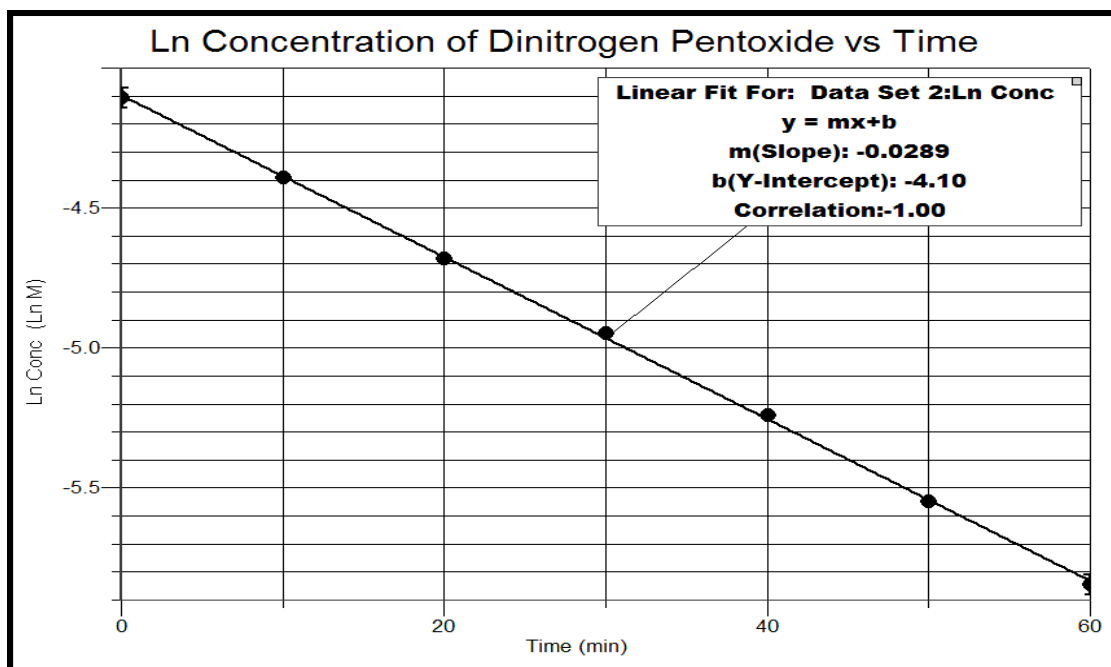
Q2: From the data given below determine the reaction order for the decomposition reaction, $2 \text{N}_2\text{O}_{5(\text{g})} \rightarrow 4 \text{NO}_{2(\text{g})} + \text{O}_{2(\text{g})}$

	Time (min) →	0	10	20	30	40	50	60
i	$[\text{N}_2\text{O}_5] \rightarrow$	0.0165	0.0124	0.0093	0.0071	0.0053	0.0039	0.0029
ii	$\ln[\text{N}_2\text{O}_5] \rightarrow$	-4.104	-4.390	-4.678	-4.948	-5.240	-5.548	-5.843
iii	$1/[\text{N}_2\text{O}_5] \rightarrow$	60.6	80.6	108	141	189	256	345

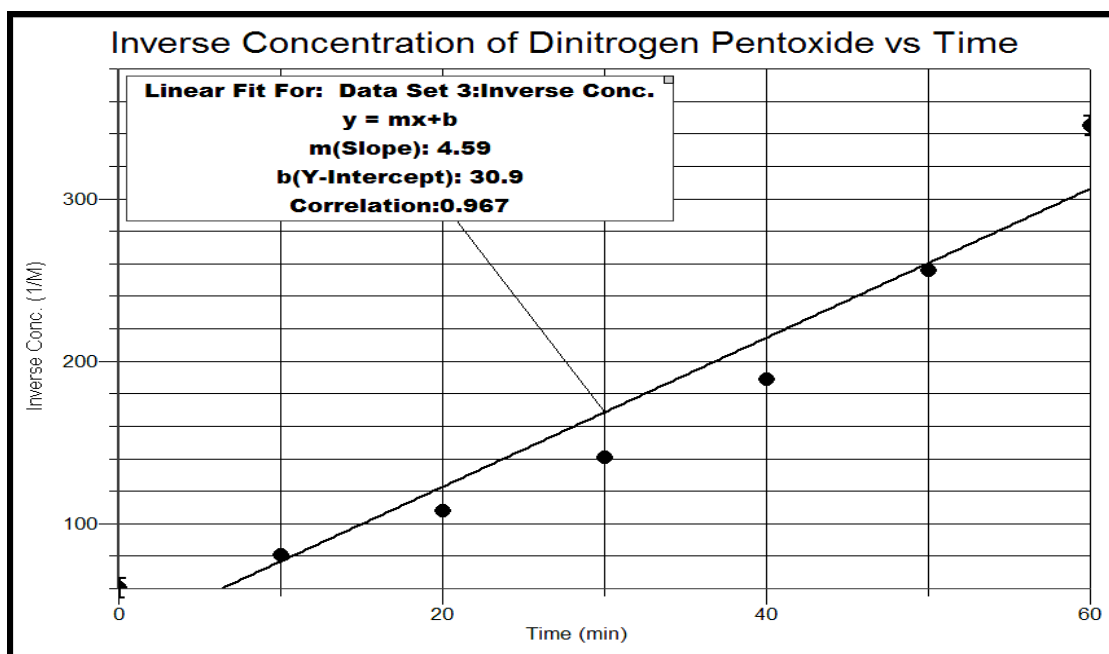
A2: i) $\text{Rate} = k[\text{N}_2\text{O}_5]^0$



ii) $\text{Rate} = k[\text{N}_2\text{O}_5]^1$



iii) Rate = $k[\text{N}_2\text{O}_5]^2$



It's first order [the second graph is the proof... the data fits!]

E) Using Integrated Rate Laws to Find Half-Life

The half-life ($t_{1/2}$) of a reaction is the amount of time required for the reactant concentration to reach half of its initial value.

Thus at the half-life, $[\text{A}]_t = [\text{A}]_0/2$

For a zero order reaction: $t_{1/2} = \frac{[\text{A}]_0}{2k}$ Take: $[\text{A}]_t - [\text{A}]_0 = -kt$ and set $[\text{A}]_t = [\text{A}]_0/2$

For a 1st order reaction: $t_{1/2} = \frac{0.693}{k}$ Take: $\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$ and set $[\text{A}]_t = [\text{A}]_0/2$

For a 2nd order reaction $t_{1/2} = \frac{1}{[\text{A}]_0 k}$ Take: $\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = kt$ and set $[\text{A}]_t = [\text{A}]_0/2$

Q3: Cyclopropane is unstable and decays over time to propene. At 1000°C, the rate constant is 9.2 s^{-1} . What is the half-life of this reaction? *Since the units of the rate constant are s^{-1} , then the reaction must be first order!*

A3: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{9.2} = 0.075 \text{ s}$

Q4: At 580. K, the following data were collected for the reaction:



Time (s)	[HI] (mM)
0	1000.
1000.	112
2000.	61
3000.	41

Based on the data, determine (i) the rate law, (ii) the value of the rate constant, and (iii) the concentration of HI at 4000. seconds.

A4: (i) One way to solve this is to find the graph which linearizes the data. A second way to solve this is to calculate the slope between consecutive data pairs.

Time (s)	[HI] (mM)	ln[HI] (mM)	1/[HI] (mM)
0	1000.	6.91	0.001000
	$\Delta[\text{HI}]/t = -0.888$	$\Delta \ln[\text{HI}]/t = -0.00219$	$\Delta 1/[\text{HI}]/t = 7.93 \times 10^{-6}$
1000.	112	4.72	0.00893
	$\Delta[\text{HI}]/t = -0.051$	$\Delta \ln[\text{HI}]/t = -0.00062$	$\Delta 1/[\text{HI}]/t = 7.07 \times 10^{-6}$
2000.	61	4.1	0.016
	$\Delta[\text{HI}]/t = -0.020$	$\Delta \ln[\text{HI}]/t = -0.00040$	$\Delta 1/[\text{HI}]/t = 8.0 \times 10^{-6}$
3000.	41	3.7	0.024

Since the slope values of $1/[\text{HI}]/t$ are reasonably the same, then the reaction must be...

2^{nd} order in HI.

(ii) The value of the rate constant is the average of the slopes:

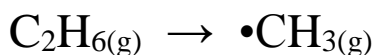
$$k = 7.7 \times 10^{-6} \text{ mM}^{-1} \text{ s}^{-1}$$

(iii) $\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = kt$

$$\frac{1}{[\text{X}]_t} - \frac{1}{[1000 \text{ mM}]_0} = [7.7 \times 10^{-6} \text{ mM}^{-1} \text{ s}^{-1}][4000 \text{ s}]$$

$$\boxed{\text{X} = 31 \text{ mM}}$$

Q5: At 700.°C, the following data were collected for the reaction:



Time (s)	[C ₂ H ₆] (mM)
0	1.59
1000.	0.92
2000.	0.53
3000.	0.31

Based on the data, determine (i) the rate law, (ii) the value of the rate constant, and (iii) the concentration of C₂H₆ at 4000. sec.

A5: (i) Complete the table below.

Time (s)	[C ₂ H ₆] (mM)	ln[C ₂ H ₆] (mM)	1/[C ₂ H ₆] (mM)
0	1.59	0.464	0.629
	$\Delta[\text{C}_2\text{H}_6]/t = -0.000670$	$\Delta\ln[\text{C}_2\text{H}_6]/t = -0.000547$	$\Delta 1/[\text{C}_2\text{H}_6]/t = 0.00047$
1000.	0.92	-0.083	1.1
	$\Delta[\text{C}_2\text{H}_6]/t = -0.00039$	$\Delta\ln[\text{C}_2\text{H}_6]/t = -0.00055$	$\Delta 1/[\text{C}_2\text{H}_6]/t = 0.00080$
2000.	0.53	-0.63	1.9
	$\Delta[\text{C}_2\text{H}_6]/t = -0.00022$	$\Delta\ln[\text{C}_2\text{H}_6]/t = -0.00057$	$\Delta 1/[\text{C}_2\text{H}_6]/t = 0.0013$
3000.	0.31	-1.2	3.2

Since the slope values of $\ln[\text{C}_2\text{H}_6]/t$ are reasonably the same, then the reaction must be...

1st order in C₂H₆.

(ii) The value of the rate constant is the average of the **negative** slopes:

$$k = 0.00056 \text{ s}^{-1}$$

(iii) $\ln[A]_t - \ln[A]_0 = -kt$

$$\ln[A]_t - \ln[1.59 \text{ mM}]_0 = -[0.00056 \text{ s}^{-1}][4000. \text{ s}]$$

$$X = 0.17 \text{ mM}$$

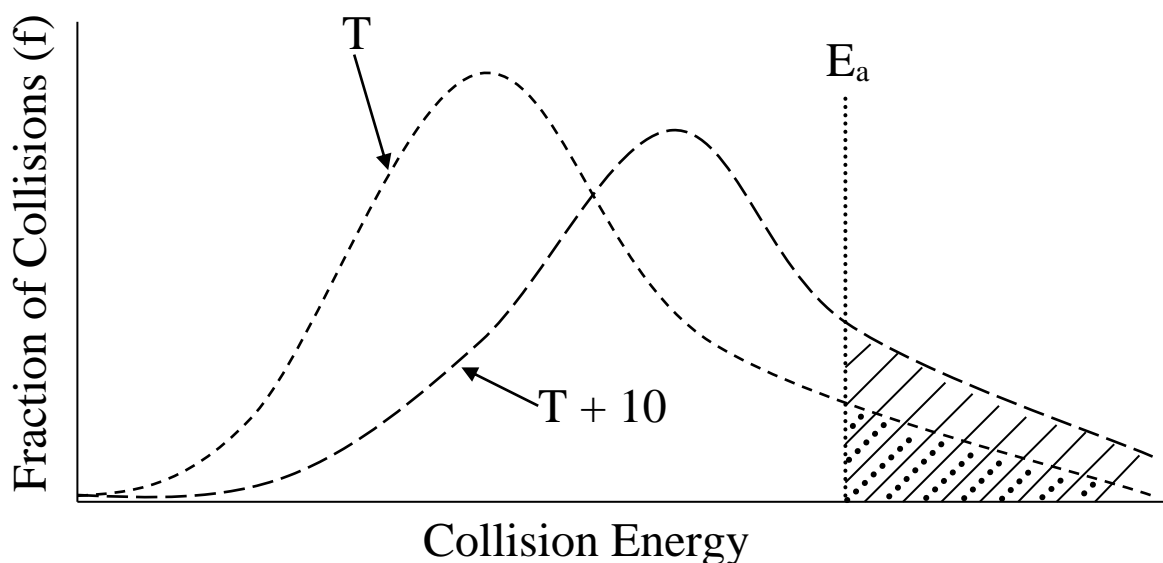
Chapter-14

Lesson-3

IV – Temperature and Rate

A) Activation Energy

- The minimum energy needed to start a reaction is called the activation energy.
- In general, reaction rate increases as temperature increases.
- Each 10°C increase approximately doubles the reaction rate.



- At a given temperature, the fraction (f) of collisions with energy greater than or equal to the activation energy (E_a) is given by...

$$f = e^{-E_a/RT}$$

- Collision energy is not the only factor that determines reaction rate. Collision frequency (Z) and proper orientation (p) also influence reaction rate. Together they combine to create a term called the frequency factor (A).

$$A = pZ$$

- The rate constant (k) for a reaction is equal to (Af) or (pZf) or...

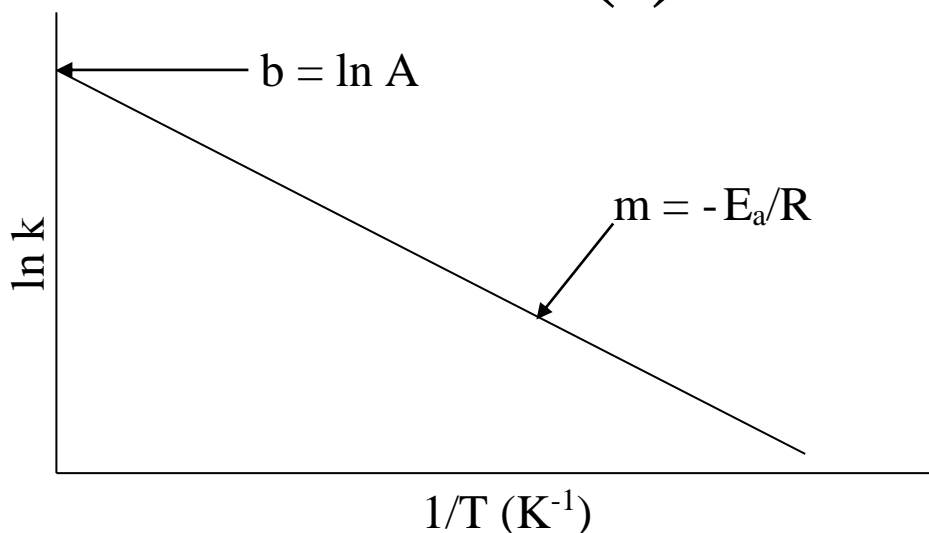
$$k = Ae^{-E_a/RT} \quad (\text{Arrhenius equation})$$

- Taking the natural log of both sides of the Arrhenius equation...

$$\ln k = \frac{-E_a}{RT} + \ln A$$

or

$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A$$



Thus:

$$E_a = -mR$$

- The two-point equation is...

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Q1: Suppose the rate of a reaction doubles when the temperature is increased from 25.0°C to 35.0°C. What is the E_a in kJ/mol?

A1: $\ln (k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1)$

$$\ln (2/1) = (-E_a/8.314)(1/308 - 1/298)$$

$$E_a = 52900 \text{ J/mol} \rightarrow \boxed{52.9 \text{ kJ/mol}}$$

Q2: The E_a for the decomposition of HCOOH at 838 K is 184 kJ/mol. What temperature would double the rate of this reaction?

A2: $\ln (k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1)$

$$\ln (2/1) = (-184000/8.314)(1/T_2 - 1/838)$$

$$T_2 = \boxed{861 \text{ K}}$$

Q3: Suppose a reaction's rate constant (k_1) is 0.0251 s^{-1} at 0.0°C . If the activation energy is 116 kJ/mol , then what is (k_2) at 100.0°C ?

A3: $\ln(k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1)$

$$\ln(k_2/0.0251) = (-116000/8.314)(1/373.0 - 1/273.0)$$

$$k_2 = \boxed{22400 \text{ s}^{-1}}$$

B) Collision Theory

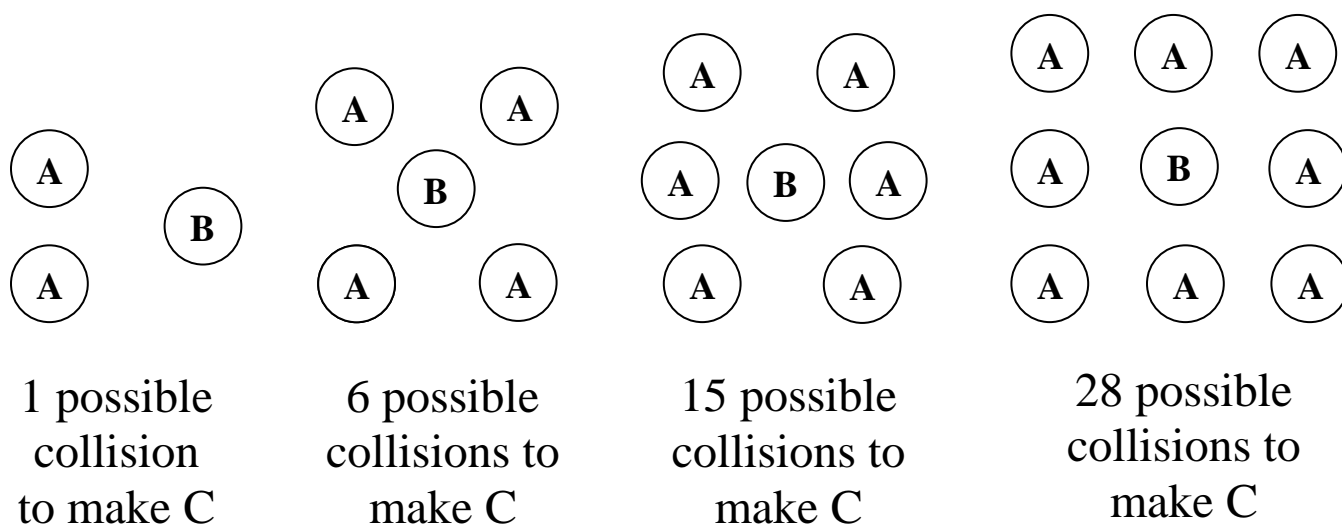
Chemical reactions ordinarily occur as a result of effective collisions between reacting particles. This is the basic tenet of collision theory.

- 1) Reacting particles must collide.
(Z = collision frequency).

Consider the reaction $2 \text{ A} + \text{B} \rightarrow \text{C}$

$$\# \text{ collisions} = \frac{n(n-1)}{2}$$

where $n = \# \text{ A's}$



- 2) Reacting particles must collide with a proper orientation.
(p = orientation probability factor)

$p \approx 1$ for reactions between individual atoms

$p \approx 10^{-3}$ for small molecules

$p \approx 10^{-6}$ (or smaller) for large molecules

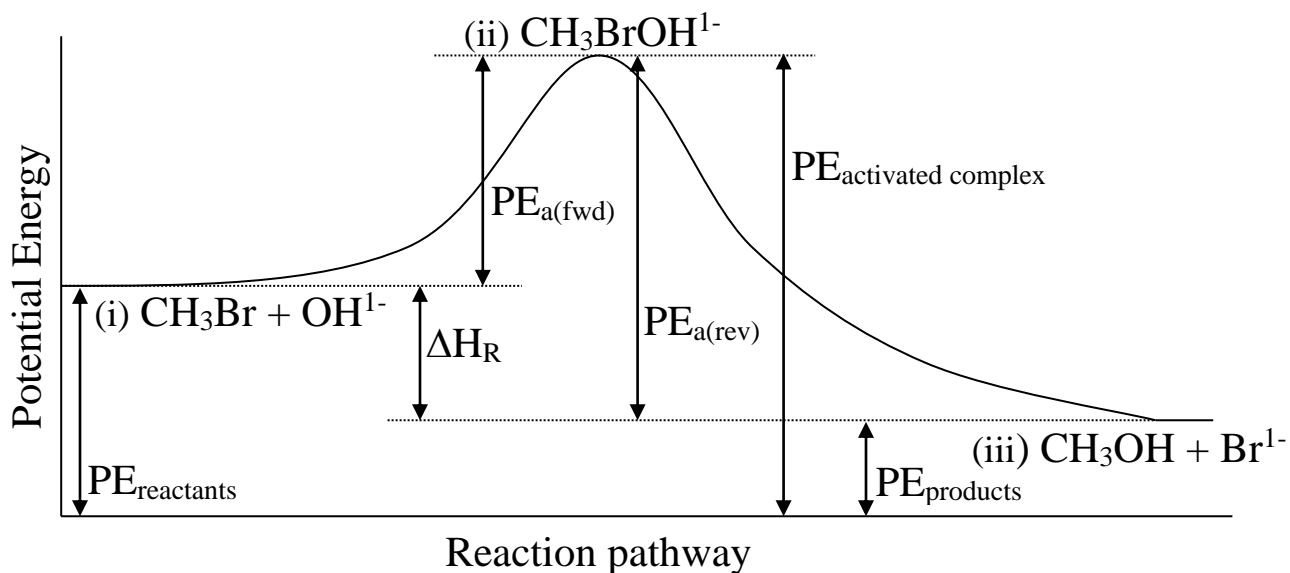
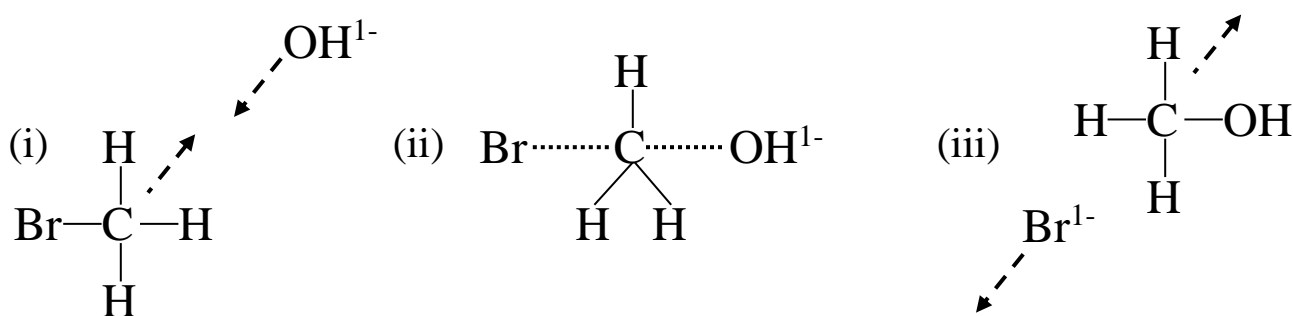
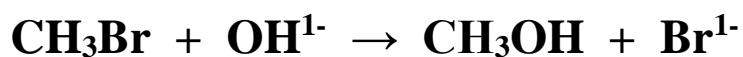
- 3) Reacting particles must collide with a minimum energy (E_a).
(f = fraction of collisions with sufficient minimum energy)

$$f = e^{-E_a/RT}$$

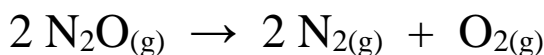
C) Transition State Theory and Reaction Diagrams

The internal energy of a system is the sum of all its KE and PE. Two reactant particles that are far apart but speeding toward each other have high KE and low PE. As the particles get closer, some KE is converted to PE as their electron clouds repel each other. At the moment of collision the PE reaches its maximum.

- 1) If the PE of collision is less than the E_a , then no reaction occurs, the particles recoil, and their KE's increase as their PE's decrease and they zoom apart unchanged.
- 2) If the PE of collision is equal to or greater than the E_a , then a reaction occurs and product particles are created. However, at the moment of collision, an extremely unstable (high PE) particle is formed. It is called the **activated complex** or **transition state**. The nature of this species is difficult to determine but it is believed that the bonds, both old and new, are stretched and deformed.



Q4: The rate constant for the reaction below is 0.38 s^{-1} at $1000. \text{ K}$



At $1030. \text{ K}$ the rate constant is 0.87 s^{-1} . (i) Calculate the activation energy for the reaction in kJ/mol . (ii) Calculate the rate constant at 273 K .

A4: (i) $\ln (k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1)$

$$\ln (0.87/0.38) = (-E_a/8.314)(1/1030. - 1/1000.)$$

$$0.83 = -E_a(-0.0000035)$$

$$E_a = 240000 \text{ J} \rightarrow \boxed{240 \text{ kJmol}}$$

(ii) $\ln (k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1)$

$$\ln (k_2) - \ln(0.38) = (-240000 /8.314)(1/273 - 1/1000.)$$

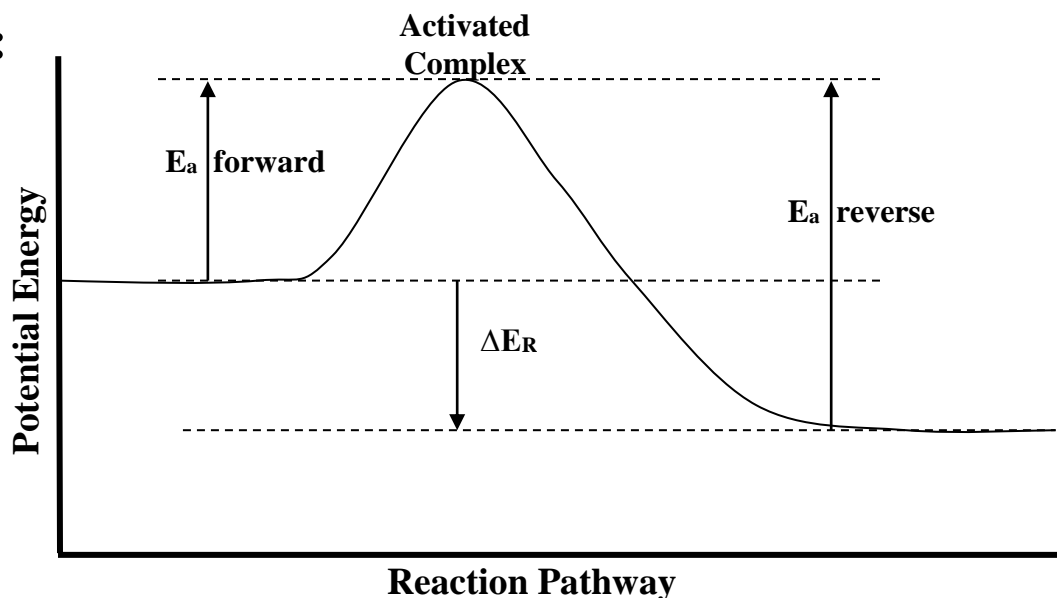
$$\boxed{k_2 = 1.5 \times 10^{-34} \text{ s}^{-1}}$$

Q5: The activation energy for a certain reaction is 125 kJ/mol and the activation energy for the reverse reaction is 155 kJ/mol .

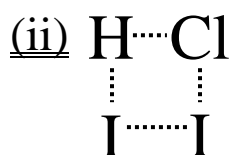
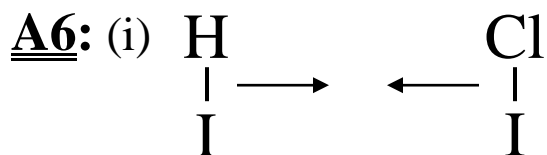
(i) Draw a reaction profile for the reaction and include

(ii) the forward E_a , (iii) the reverse E_a , (iv) the energy of reaction ΔE_R , and (v) the location of the activated complex.

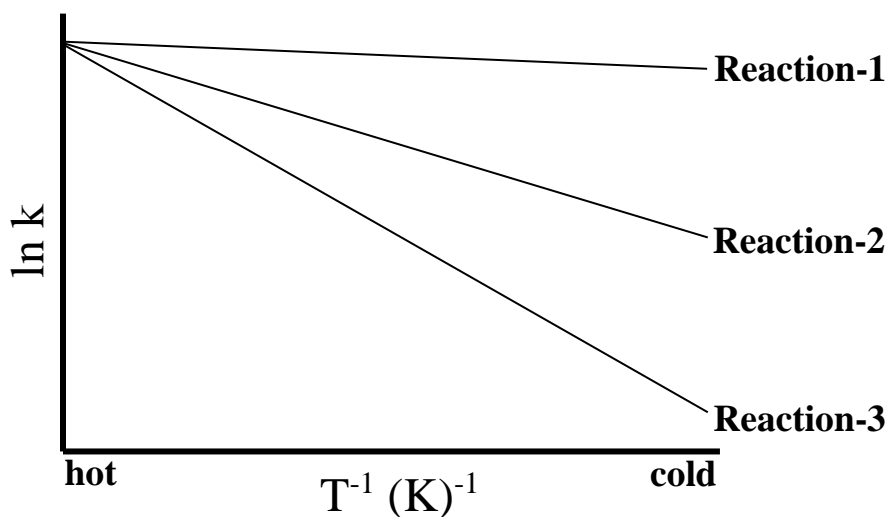
A5:



Q6: The reaction $\text{HI}_{(\text{g})} + \text{ICl}_{(\text{g})} \rightarrow \text{I}_{2(\text{g})} + \text{HCl}_{(\text{g})}$ occurs in a single step. (i) Draw a diagram showing how the two molecules should approach each other so as to result in a collision with the correct orientation. (ii) Draw the transition state (activated complex) for the atoms once the collision has occurred. Use dotted lines to show bonds that are in transition (breaking and forming).



Q7: The diagram below represents a graph of $\ln k$ vs $T^{-1} (\text{K})^{-1}$.
 (i) What is the significance of the value of the slope of the curve for each reaction? (ii) Which reaction has the lowest sensitivity to changes in temperature? (iii) Which reaction has the highest activation energy?



A7: (i) $\text{slope} = -(E_a \text{ of the reaction in Joules}) \div (8.314 \text{ J/mol}\cdot\text{K})$

(ii) Reaction-1: As temperature changed, its values for k changed the least.

(iii) Reaction-3: Its graph has the largest slope.

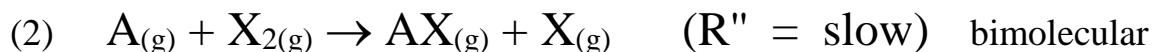
Chapter-14

Lesson-4

V - Reaction Mechanism

- Most reactions take place in a series of elementary steps called the **reaction mechanism**.
- The elementary steps of the reaction mechanism must add up to the overall reaction.
- The slowest elementary step in the reaction mechanism is called the **rate-determining step**.
- An elementary step with a single reactant is called **unimolecular**.
- An elementary step with two reactants is called **bimolecular**.
- An elementary step with three reactants is called **termolecular**.
Termolecular reactions are improbable and thus very rare!
- The rate law for an elementary step depends on the **molecularity** (number of reacting molecules) of that step.
- For any elementary step in the reaction mechanism, the order with respect to each reactant is its coefficient in that step.
- To find the overall rate expression for a multi-stepped mechanism
 - (1) Focus on the slowest step in the mechanism. Assume that the rate for that step equals the overall rate.
 - (2) Write the rate expression for the slowest step. Be sure that the order with respect to each reactant is its coefficient.
 - (3) Eliminate any unstable intermediates from the rate law expression. This is usually achieved by substituting the equilibrium expression from a fast step that occurs before the slow step.
 - (4) Any fast elementary step after the rate-determining step will have no effect on the rate law of the reaction.
 - (5) For a mechanism to be valid, its rate law must be supported by observation and data.

Q1: Consider the reaction, $A_{2(g)} + X_{2(g)} \rightarrow 2 AX_{(g)}$ which has the following reaction mechanism:



Determine the rate expression for this reaction.

A1: The slow step has the rate expression: $R'' = k''[A][X_2]$

However, the species **A** must be an unstable intermediate and thus cannot remain in the overall rate expression since it is not found in the net reaction equation.

Step-1 is an equilibrium step ... $A_{2(g)} \rightleftharpoons 2 A_{(g)}$

and ... $R'_{\text{forward}} = k'_{\text{forward}}[A_2]$ and $R'_{\text{reverse}} = k'_{\text{reverse}}[A]^2$.

At equilibrium ... $R'_{\text{forward}} = R'_{\text{reverse}}$,

and thus ... $k'_{\text{forward}}[A_2] = k'_{\text{reverse}}[A]^2$!

Solving for $[A]$, the expression becomes $[A] = (k'_{\text{for.}}/k'_{\text{rev.}})^{1/2}[A_2]^{1/2}$.

Substituting into the slow step rate expression ...

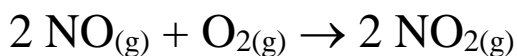
$R'' = k''[A][X_2]$ becomes...

$$R = k''(k'_{\text{for.}}/k'_{\text{rev.}})^{1/2}[A_2]^{1/2}[X_2]$$

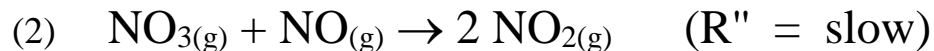
$$R = \underline{k}[A_2]^{1/2}[X_2]$$

NOTE: The ratio $k'_{\text{forward}}/k'_{\text{reverse}}$ is actually the equilibrium constant, K'_{eq} , for step-1. Recall from first year chemistry, that an equilibrium constant (K_{eq}) is the ratio of the molar concentration of the products over the molar concentration of the reactants raised to the exponent equal to their coefficients.

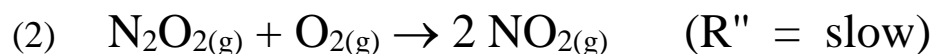
Q2: The following two mechanisms are proposed for the reaction



Mechanism-1:



Mechanism-2:



Show that each of these mechanisms is consistent with the experimentally observed rate law...

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

A2: Mechanism-1:

$$\begin{aligned} \text{R}'' &= k''[\text{NO}_3][\text{NO}] && \text{but } \text{NO}_3 \text{ is an intermediate species so...} \\ K' &= \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]} \rightarrow [\text{NO}_3] = K'[\text{NO}][\text{O}_2] \end{aligned}$$

$$\text{R} = k''K'[\text{NO}][\text{O}_2][\text{NO}]$$

$$\text{R} = \boxed{k[\text{NO}]^2[\text{O}_2]}$$

Mechanism-2:

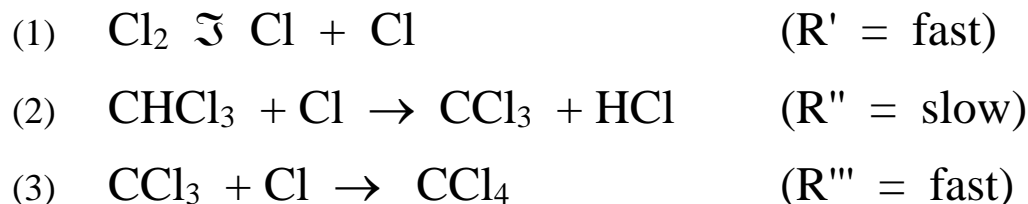
$$\begin{aligned} \text{R}'' &= k''[\text{N}_2\text{O}_2][\text{O}_2] && \text{but } \text{N}_2\text{O}_2 \text{ is an intermediate species so...} \\ K' &= \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \rightarrow [\text{N}_2\text{O}_2] = K'[\text{NO}]^2 \end{aligned}$$

$$\text{R} = k''K'[\text{NO}]^2[\text{O}_2]$$

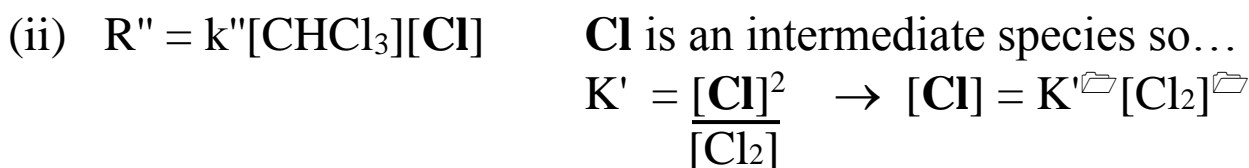
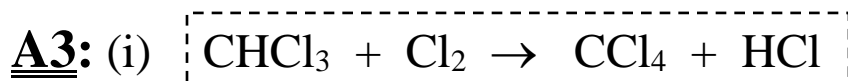
$$\text{R} = \boxed{k[\text{NO}]^2[\text{O}_2]}$$

Both mechanisms are consistent and plausible with respect to their molecularity and the observed rate law. The detection of either of the two intermediates is now in order.

Q3: The following mechanism has been proposed for the reaction between chlorine and chloroform:



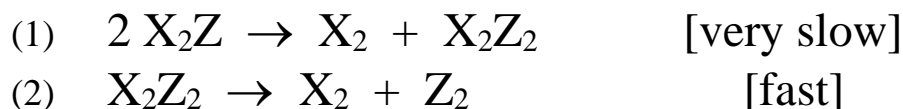
- Write the net reaction.
- Write the rate law implied by this mechanism.



$$\text{Rate} = K' k'' [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$$

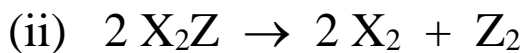
$$\text{Rate} = k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$$

Q4: The reaction is very slow and occurs via the following proposed two step mechanism:



- What is the molecularity of each step in the proposed reaction mechanism?
- Write the net reaction.
- In the reaction, what is X_2Z_2 ?
- Write the rate law implied by this mechanism.

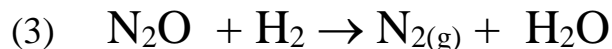
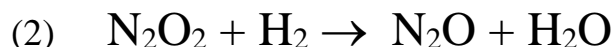
A4: (i) Step-1 is bimolecular and step-2 is unimolecular.



(iii) X_2Z_2 is a reaction intermediate.

(iv) $\text{R} = k[\text{X}_2\text{Z}]^2$

Q5: The rate law of the reaction $2 \text{NO}_{(g)} + 2 \text{H}_{2(g)} \rightarrow \text{N}_{2(g)} + 2 \text{H}_2\text{O}_{(g)}$ is **rate** = $k[\text{NO}]^2[\text{H}_2]$, and the proposed mechanism is:



Which step in the mechanism is likely to be the rate determining step and why?

A5: Step-2 is the rate determining step...

... **if** step-1 is a rapid equilibrium step and **if** step-3 is fast.

$$R'' = k''[\text{N}_2\text{O}_2][\text{H}_2]$$

N_2O_2 is an intermediate species so

$$K' = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \rightarrow [\text{N}_2\text{O}_2] = K' [\text{NO}]^2$$

$$\text{Rate} = K'k''[\text{NO}]^2[\text{H}_2]$$

$$\boxed{\text{Rate} = k[\text{NO}]^2[\text{H}_2]}$$

Q6: The following mechanism has been proposed for the reaction between hydrogen gas and iodine vapor:



Is this proposed mechanism consistent with the rate law below:

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

A6: $R'' = k''[\text{H}_2][\text{I}]$

rate law for the step-2 (slow step)

$$K' = [\text{I}]^2/[\text{I}_2]$$

equilibrium expression for step-1

$$[\text{I}] = K'^{1/2} \times [\text{I}_2]^{1/2}$$

equilibrium expression for step-1

$$\text{Rate} = k[\text{H}_2][\text{I}_2]^{1/2}$$

rate law based on proposed mechanism

No, the proposed mechanism is NOT consistent with the rate law.

Chapter-14

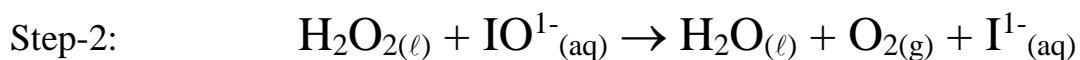
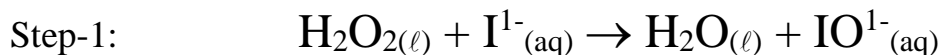
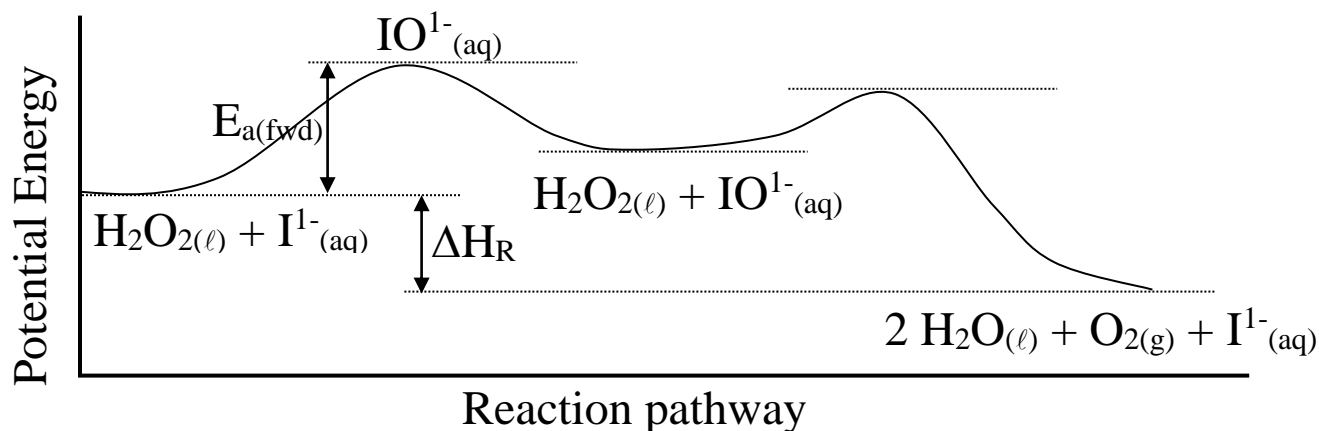
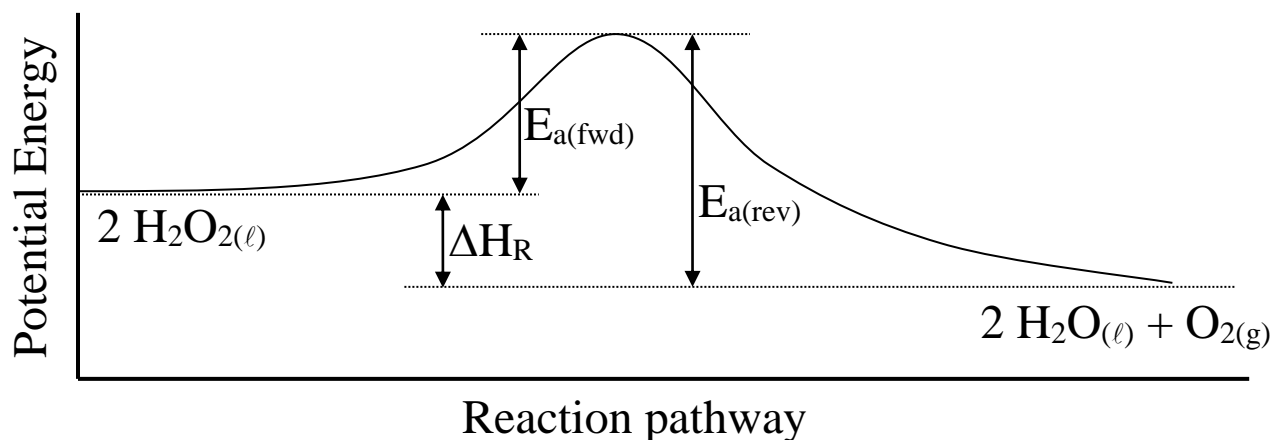
Lesson-5

VI - Catalysis

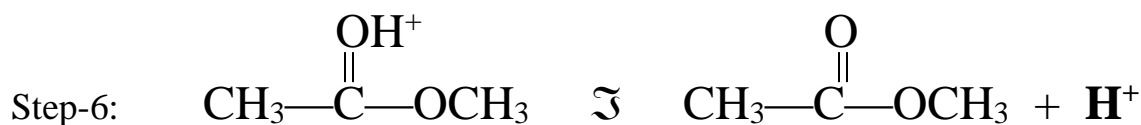
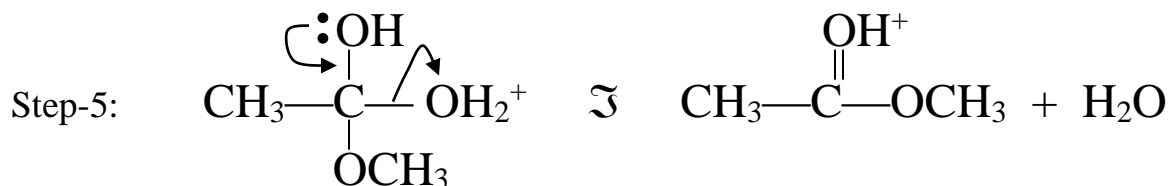
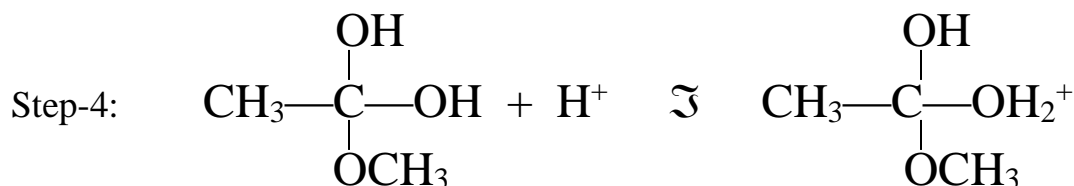
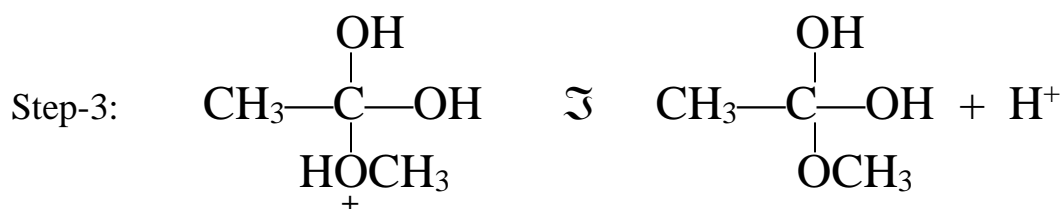
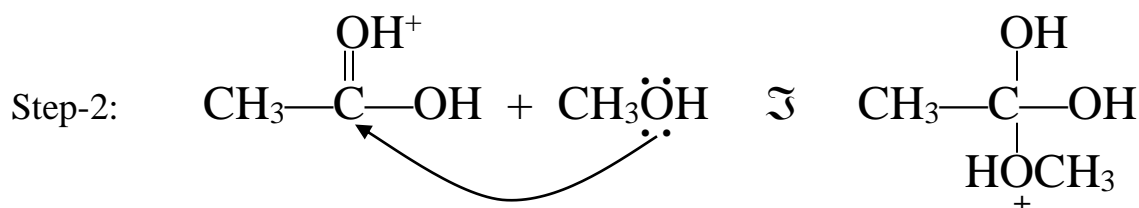
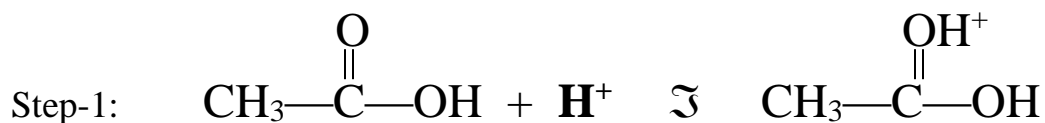
- A **catalyst** increases the rate of a reaction by providing a reaction pathway with lower activation energy.
- A catalyst is not consumed during the reaction.
- A catalyzed reaction does NOT produce more product than an uncatalyzed reaction, but produces the product more quickly.

A) Homogeneous Catalysis of the Decomposition of H₂O₂

- A **homogeneous catalyst** is one that exists in the same phase (usually in solution) as the reactants.



- **Acid-base catalysis**, in which a reactant either gains or loses a proton, is a specific example of **homogeneous catalysis**.
- The mechanism for the **acid-catalyzed** esterification reaction of acetic acid and ethanol is shown below. The catalyst, H_2SO_4 , is often used to catalyze dehydration synthesis reactions.

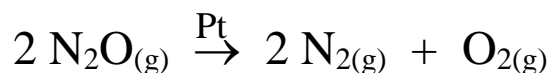


B) Heterogeneous Catalysis of the Decomposition of HI

- A **heterogeneous catalyst** (often a solid) exists in a different phase from the reactants (usually liquids or gases).
- Finely divided metals, such as nickel, silver, gold, platinum, or palladium, are used as catalysts. These metals provide a surface for the reactants to meet and rearrange with less activation energy so these metals are **surface catalysts**.
- Hydrogen iodide gas (HI) decomposes on gold.

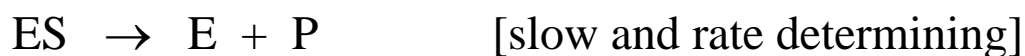


- Dinitrogen monoxide gas (N₂O) decomposes on platinum.



C) Enzymes

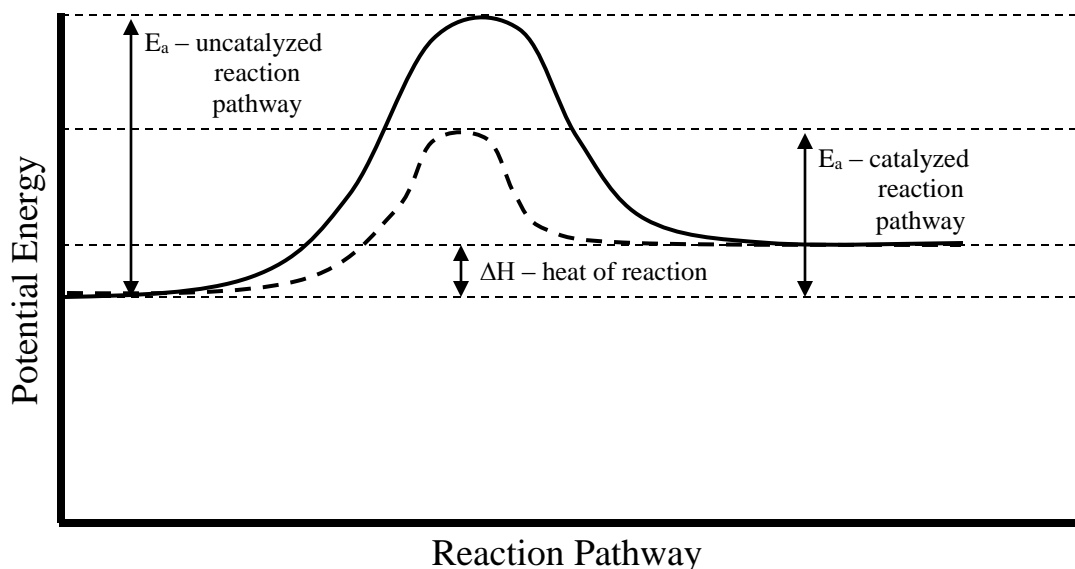
- An organic catalyst is called an **enzyme**. Enzymes are proteins of high molar mass (between 15,000 g/mol and 1,000,000 g/mol).
- Enzymes work by providing an **active site** for the **substrates** (reactants) to meet.
- The substrates are held in the active site by intermolecular forces forming the stabilized **enzyme-substrate complex**.
- The enzyme-substrate complex (ES) then decomposes to form the product (P) and returns the enzyme (E) to its original state.



- Enzymes are extremely specific: one enzyme to one reaction!
- Two models explain the enzyme-substrate specificity:
 - **Lock-and key model**: The substrate (*key*) fits exactly into the active site (*lock*). *One lock for each key!*
 - **Induced-fit-model**: The enzyme changes shape as the substrate lands at the active site inducing a perfect fit.

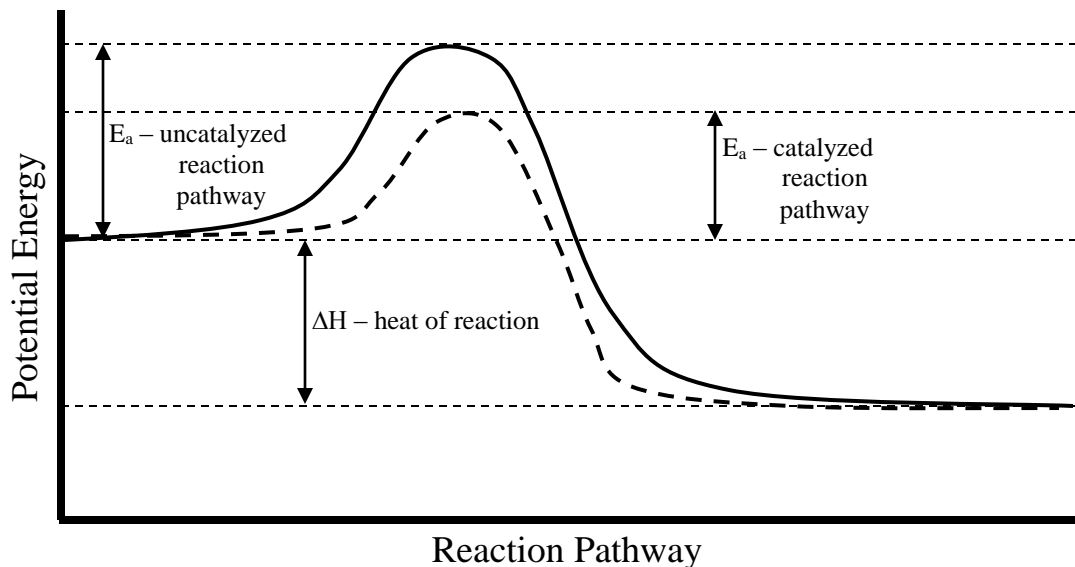
Q1: For a certain reaction whose ΔH_R is +10 kJ, the activation energy (E_a) is 50 kJ. In the presence of a catalyst, the activation energy is lowered to 30 kJ. Draw a potential energy diagram that shows the reaction pathways for both the uncatalyzed and catalyzed reactions.

A1:



Q2: The activation energy for a certain reaction is 70 kJ. In the presence of a catalyst, the activation energy is lowered to 45 kJ. If the reaction's ΔH_R is –60 kJ, then draw a potential energy diagram that shows the reaction pathways for both the catalyzed and uncatalyzed reactions.

A2:



Q3: How does a catalyst affect (i) the rate of the reverse reaction?
(ii) the ΔH for the reaction? (iii) the rate law for the reaction?
(iv) the pathway by which the reaction occurs?

A3: (i) A catalyst increases the rate of the reverse reaction.

(ii) A catalyst has no effect on the ΔH for the reaction.

(iii) A catalyst changes the rate law for the reaction.

(iv) A catalyst changes the reaction pathway to one with a lower activation energy.

Q4: A catalyst increases the rate constant (k) for a reaction by a factor of 1000. If the activation energy (E_a) for the original reaction pathway at 25.0°C is 98.0 kJ/mol, then what will be the activation energy of the new pathway, all else being equal?

A4: Let the original rate constant (k_1) equal to 1 and the rate constant (k_2) for the catalyzed reaction equal to 1000.

$\ln k_1 = -E_{a1}/RT + \ln A$ $R, T, \text{ and } "A" \text{ will be the same for both reactions.}$

$$\ln(1) = \left(\frac{-98000 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(298.0 \text{ K})} \right) + \ln A \quad \text{solve for "A".}$$

$$A = 1.51 \times 10^{17}$$

$\ln k_2 = -E_{a2}/RT + \ln A$ $\text{solve for } E_a.$

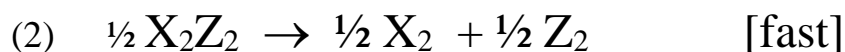
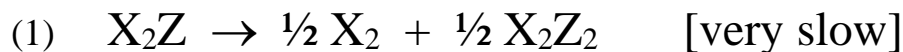
$$\ln(1000) = \left(\frac{-X}{(8.314 \text{ J/mol}\cdot\text{K})(298.0 \text{ K})} \right) + \ln(1.51 \times 10^{17})$$

$$X = 80900 \text{ J/mol} \rightarrow 80.9 \text{ kJ/mol}$$

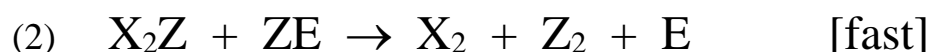
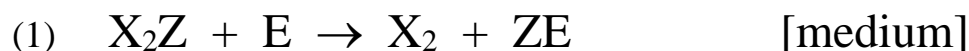
Q5: Consider the following hypothetical reaction:



This reaction is very slow and occurs via the following proposed two step mechanism:



The introduction of a catalyst into the system speeds up the reaction. A proposed two step catalyzed reaction mechanism is given below:



- (i) Verify that the elementary steps in the proposed catalyzed reaction mechanism to the overall reaction equation.
- (ii) In the catalyzed reaction, explain what species is the catalyst and what species may be reaction intermediates.
- (iii) What is the molecularity of each step of the proposed catalyzed reaction mechanism?
- (iv) Write the rate expressions for the uncatalyzed and catalyzed reactions.

A5: (i) The two step mechanism sums to $\text{X}_2\text{Z} \rightarrow \text{X}_2 + \frac{1}{2} \text{Z}_2$.

(ii) E is the catalyst because it is introduced at the beginning of the first step and it reappears unchanged at the end of the last step. ZE is a reaction intermediates because it is formed in the first step and used up in the second step.

(iii) The molecularity of both steps is two.

(v) uncatalyzed reaction: $\text{Rate} = k[\text{X}_2\text{Z}]$

catalyzed reaction: $\text{Rate} = k[\text{X}_2\text{Z}][\text{E}]$